



Biogenic safety of clay barrier materials for radioactive waste repository database



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Background

Clay minerals are widely used as materials for construction of engineered barriers for nuclear waste and spent fuel repositories all over the world due to perfect isolation properties and high sorption capacity,

Unwanted microbiological processes that occur in geological repository can cause deterioration of clay barrier materials, which may significantly affect long-term safety of the repository

Conditions for microbiological process: liquid water, electron donors and acceptors, carbon source, biogenic elements source (N,P,S etc), temperature 5-120 °C

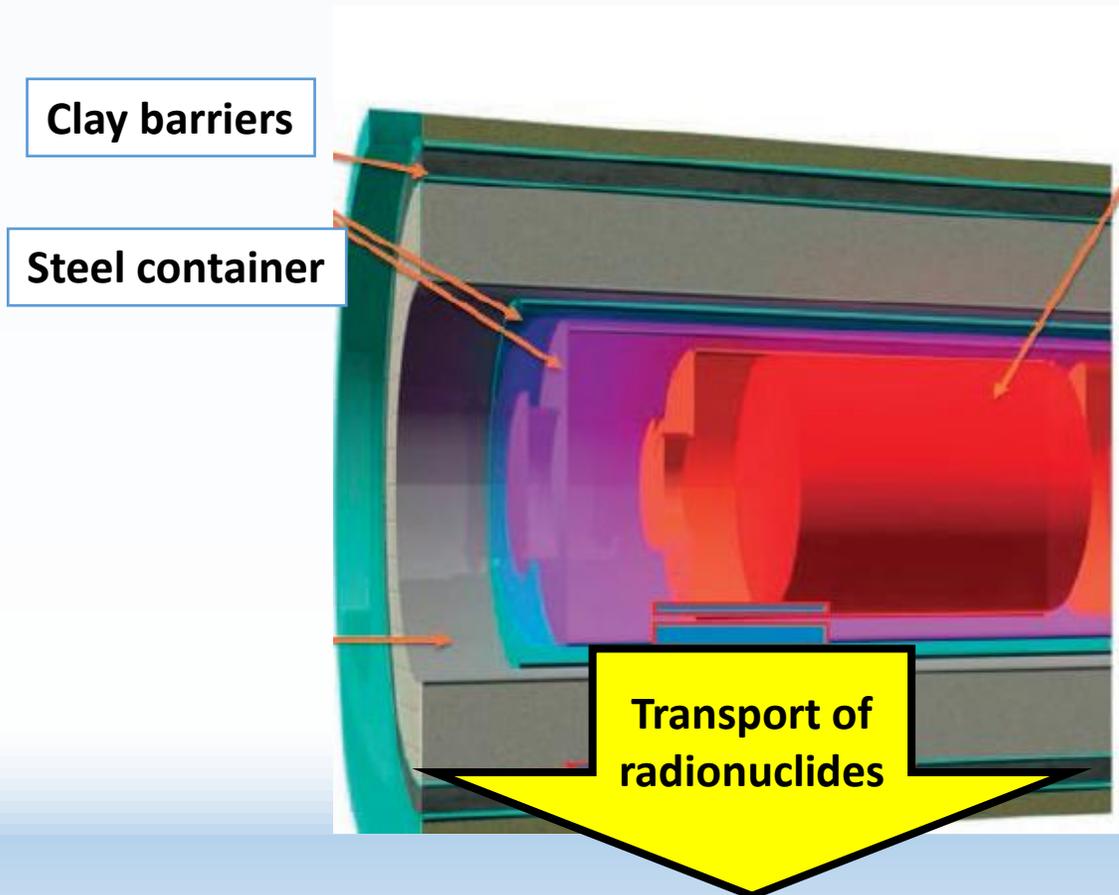
Electron donors	Acceptors	biogens
H ₂	O ₂	K,
C _{org}	Fe ⁺²	P
CO	Mn ⁺⁴	S
S ⁻²	SO ₄ ²⁻	C
S ⁰	CO ₂ ²⁻	N
Fe ⁰	NO ₃ ⁻	Ca
Fe ⁺²	UO ₂ ²⁻	+ microelements
NH ₄ ⁺		Co, Cu, Se, B...

Clays are a source of organic matter, nutrients and microorganisms, When moisture, radiolysis products, and steel get in bentonite barriers, intensification of microbial activity can occur, leading to a number of undesirable and potentially dangerous processes: gas generation, steel biocorrosion, etc,

Mineral phase	Formula
Kaolinite	Al ₂ (Si ₂ O ₅)(OH) ₄
Quartz	SiO ₂
Montmorillonite (Ca)	Ca _{0,2} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ •nH ₂ O
Montmorillonite (Na)	Na _{0,2} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ •nH ₂ O
K-spar	KAlSi ₃ O ₈
Illite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂
Calcite	CaCO ₃
Plagioclase	NaAlSi ₃ O ₈
Fe	Fe ₂ O ₃

New Russian repository conception

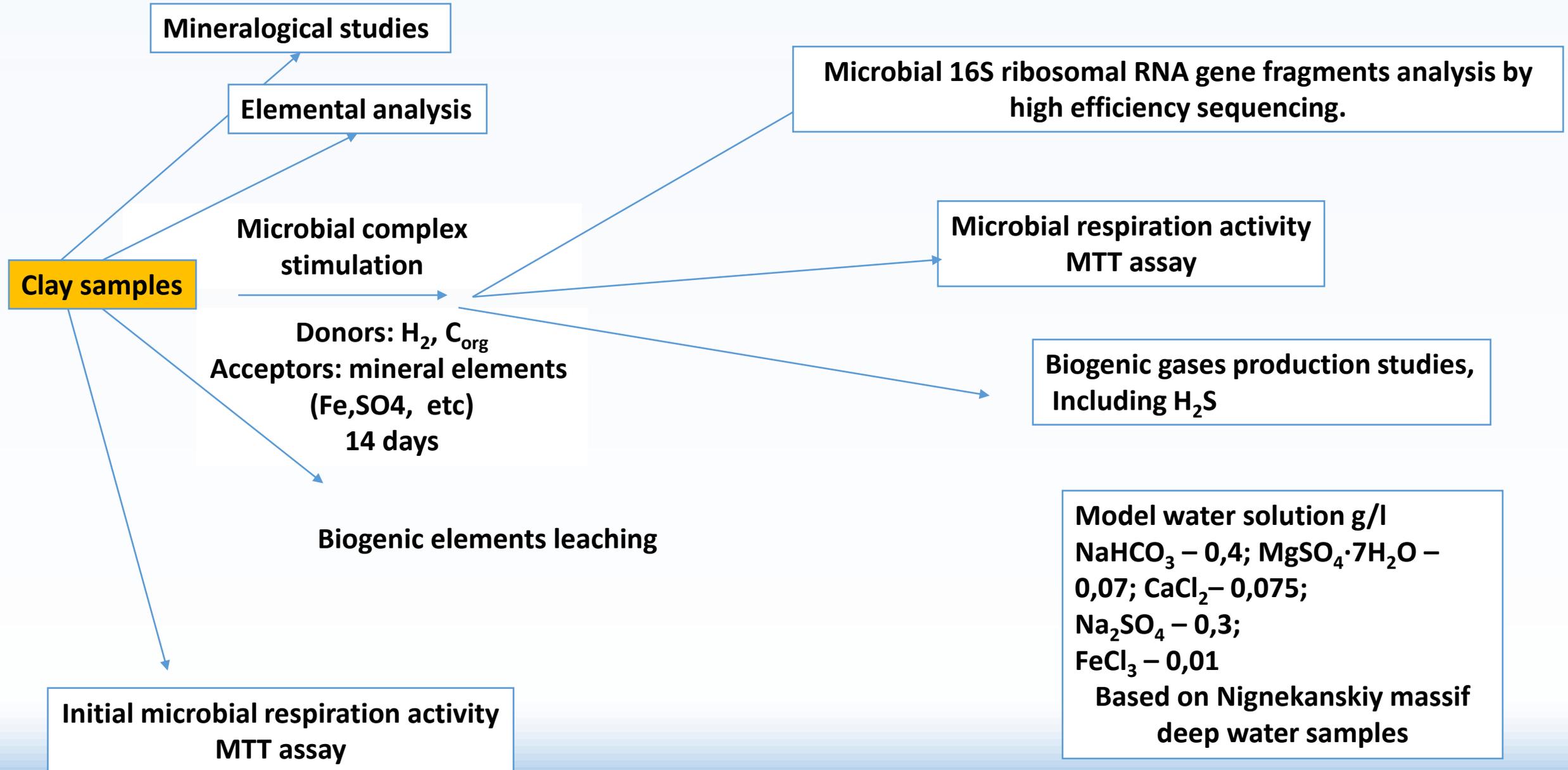
IN THE NIZHNEKANSKIY MASSIF
Krasnoyarsk region, Russia



The developed concept was used to assess clay materials found in Russian Federation that could potentially be used to construct engineered safety barriers.

Aim o this study is forming the basis for the formation of a database of microbial safety of engineering barrier materials for radioactive waste storage.

Materials and methods



Mineralogical parameters of the samples

Sample №	Sample description	Quartz	Clay minerals				Field spar		Other minerals	
			Kaolinite	Montmorillonite	Illite	Muscovite	PFS	plagioclase	calcite	anatase
2	Clay barrier TM	33,5	24	31	2	3	5	3	-	-
3	Caoline clay	25	24	15	5	-	5	6	1,5	1
5	Black clay	36	39	8	4,5	-	5,5	1,5	-	-
7	Bentonite 1	4	-	78	-	-	-	-	1,5	15
9	Bentonite 2	9	-	89,5	-	-	-	-	1,5	-
15	Bentonite 3	11,5	4	71	1	-	4	5	3	-
14	Bentonite 4	16	6	67	3	-	0,5	1,5	5	1

All samples are used or going to be in different engineering barriers. All of them are currently among the list of potential clays for barriers in **NIZHNEKANSKIY MASSIF repository**.

Clay barrier is a industrial mixture, widely used as a engineering barrier

Biogenic elements content in the samples, mass.%

Sample №	Fe	S	C	N	C/N ratio	pH of solution
2	4,54	<0,02	0,41	0,02	41,26	7,9
3	2,29	<0,02	<u>0,68</u>	0,02	22,41	7,4
5	<u>19,94</u>	<0,02	0,19	0	42,57	7,68
7	4,63	0,05	0,14	0	0	8,2
9	4,82	<0,02	0,01	0	0	6,3
15	3,36	0,04	0,34	0,01	34,2	8,5
14	<u>5,94</u>	<u>0,08</u>	<u>0,86</u>	0,03	25,2	7,4

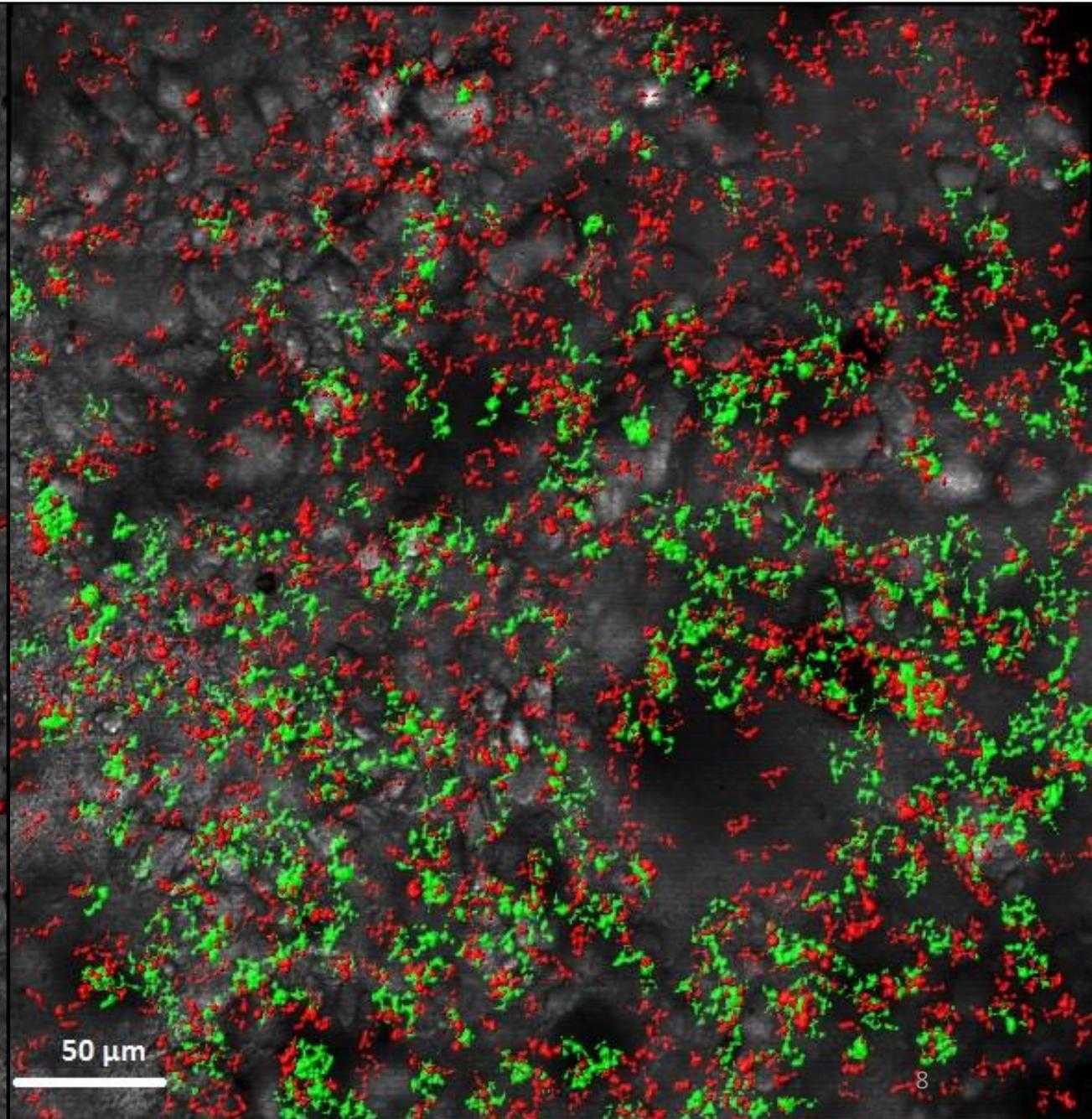
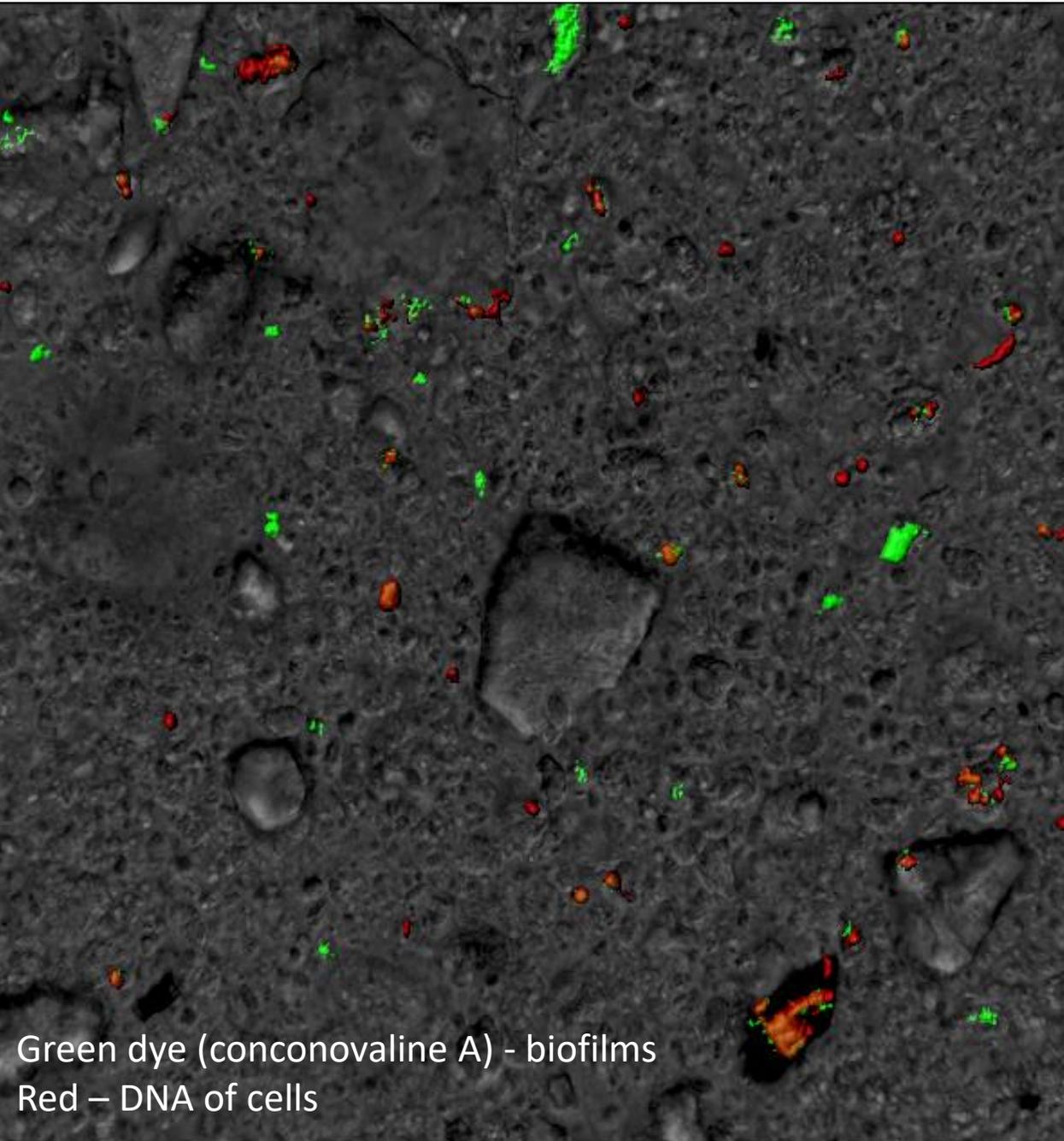
All clays were found to contain high iron, presumably in different mineral forms (goethite, oxides, siderite) with different bioavailability. Maximum organic matter was observed in 3 and 14 samples.

Biogenic elements leaching in distilled water mg/l (1 gr of dry clay)

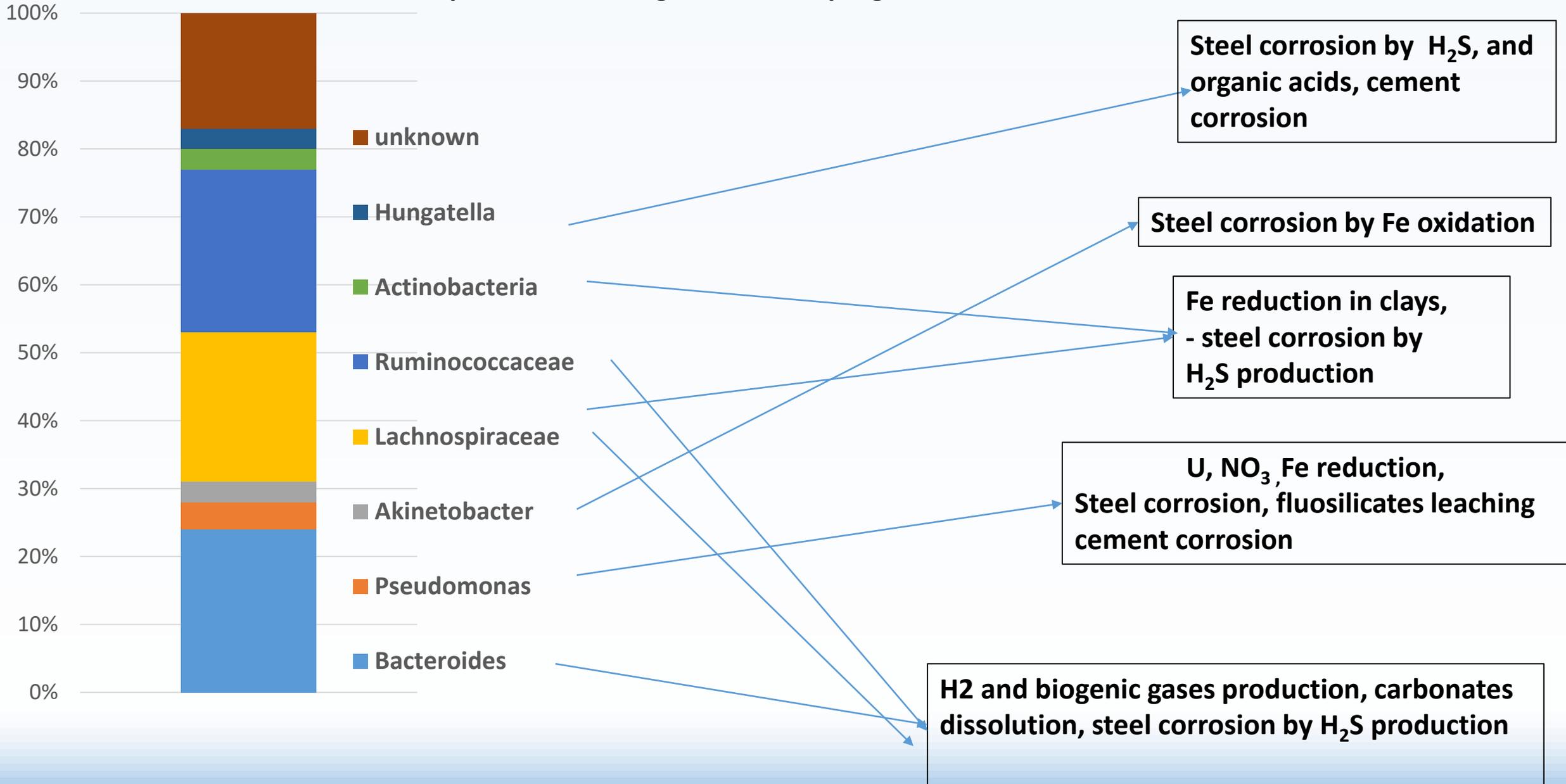
Sample No	Na	K	Ca	Mg	Fe	P	Σ leaching
2	47,06	2,9	5,7	4,4	3,5	0,24	63,8
3	13,2	4,3	40,8	10,9	0,23	0,29	69,72
5	0,58	2,1	15,2	3,4	0,28	0,14	21,7
7	284,3	1,3	5,2	11,5	28,8	0,4	331,5
9	5,2	2,3	6,1	2,9	0,6	0,06	17,16
15	106,7	7,3	2,6	3,4	2,5	0,16	122,66
14	113,7	2,2	13,5	5,9	0,33	0,001	135,631

Solutions with suitable ionic strength are necessary for the development of microorganisms. The ability of clays to partially dissolve to leach readily available ions into a solution should lead to the development of microbial processes. Thus, samples 7, 15 and 14 are potentially capable of intensifying microbial processes

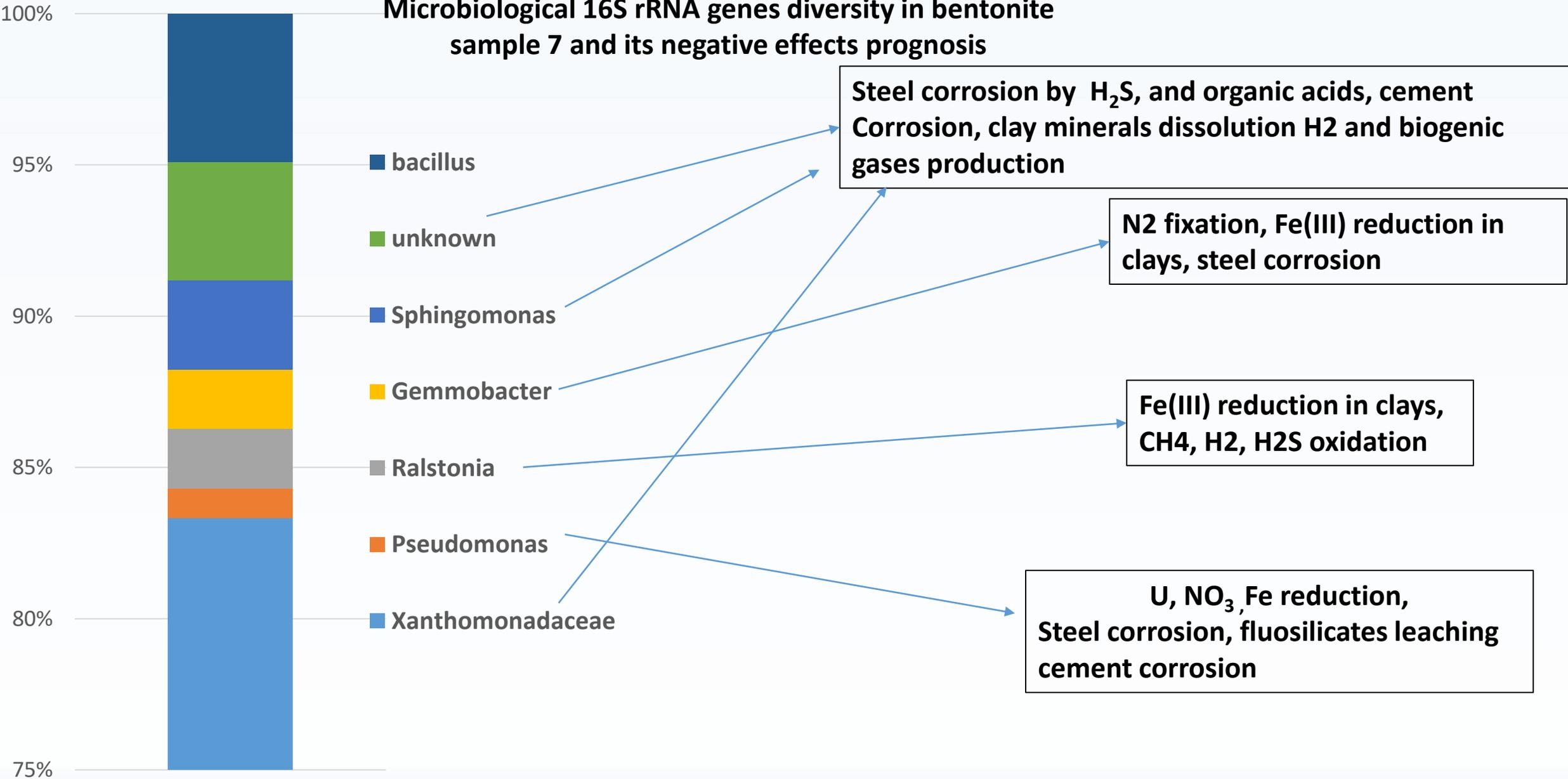
Confocal microscope photo of the biofilms on sample 15 before (left) and after (right) microbial treatment



Microbiological 16S rRNA genes diversity in bentonite sample 15 and its negative effects prognosis

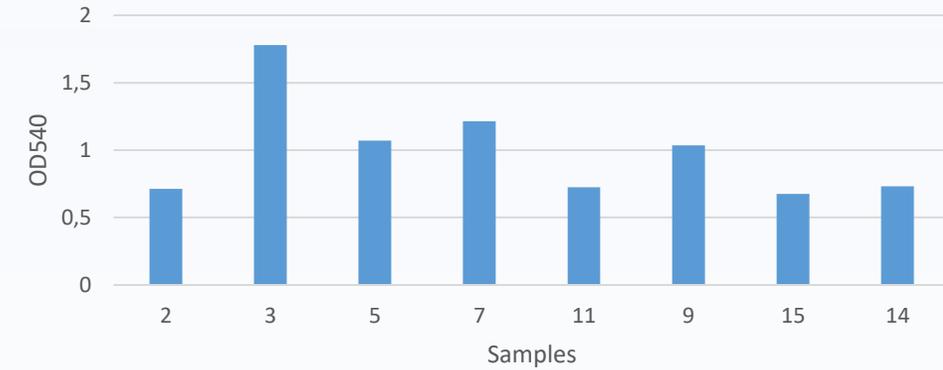
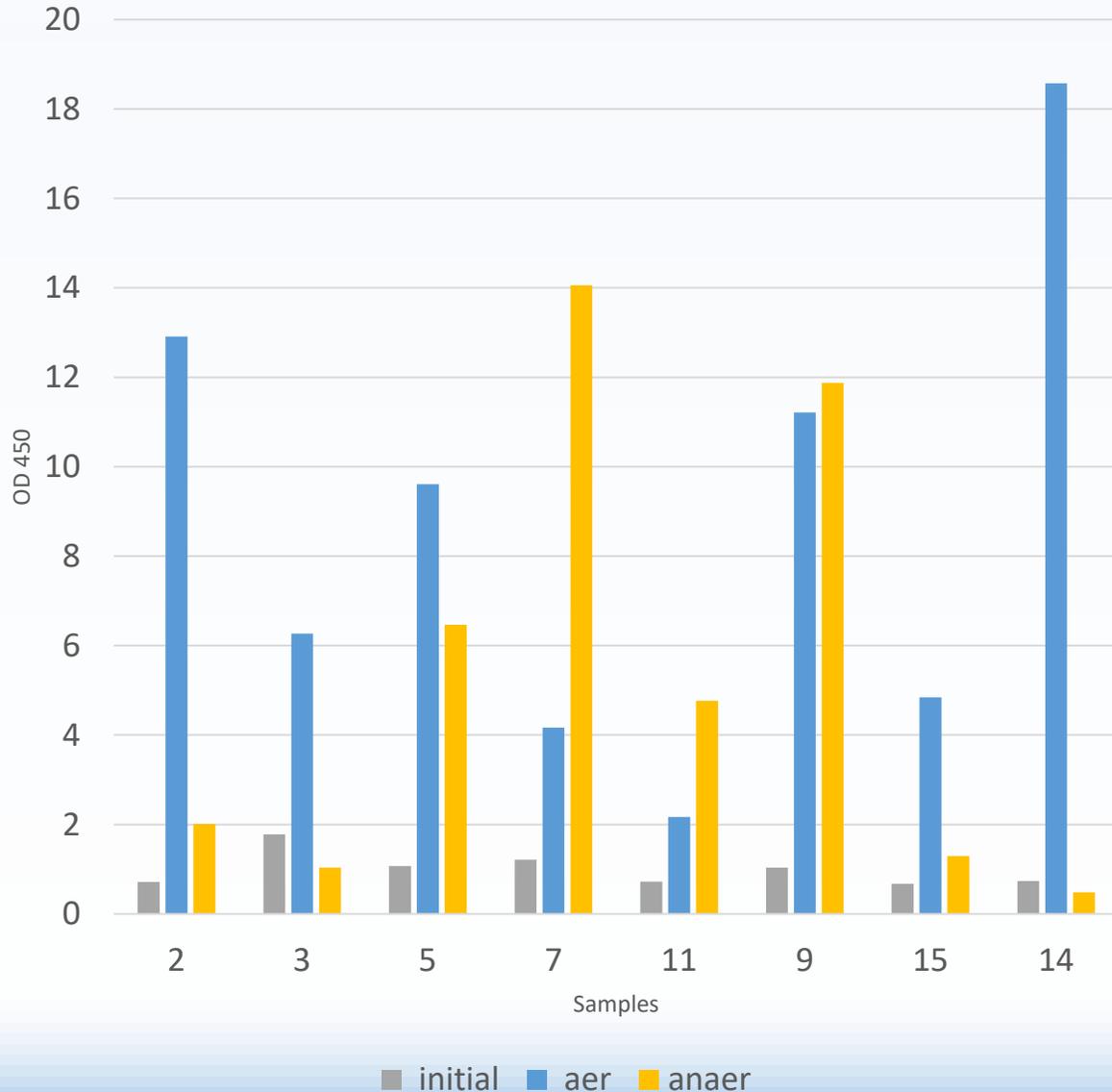


Microbiological 16S rRNA genes diversity in bentonite sample 7 and its negative effects prognosis



Microbiological 16S rRNA genes diversity in bentonite sample 7

MTT assay results before and after samples microbial complex stimulating in aerobic and anaerobic conditions



Initial MTT test for samples before stimulating shows its microbial complex activity and quantity
 Sample 3 shows the highest results

No positive correlation was found between the indices of the initial respiratory activity of the microbial complex and its activity after stimulation.

As well as no positive correlation was found between the indices of the initial respiratory activity under aerobic and anaerobic conditions

Based on the obtained data, the coefficient of microbial fouling of CMTT by respiration was introduced, which shows how many times the respiratory activity increases after stimulation, compared with the control.

H₂S production

Sample	H ₂ S concentration mg from 1g of sample	
	<u>e donor</u> sodium acetate 500 mg\l	<u>e donor</u> H2 in gaze phase
2	1,3	1,3
3	1,2	0,7
5	0,5	1,9
7	0	0
9	0,2	0,2
15	1,3	1,3
14	1,3	1,3

The microbial production of hydrogen sulfides due to the reduction of sulfate ions in formation water and sulfur compounds in the structure of clay minerals is one of the most important parameters from the point of view of storage safety. The formation of hydrogen sulfide in contact with steel can lead to its accelerated corrosion and destruction.

H ₂ S production mark			
Sample	S ²⁻ (Ac)	S ²⁻ (H2)	Σ
7	5	5	10
9	5	5	10
5	5	20	25
3	15	10	25
14	15	15	30
2	15	15	30
15	15	15	30

In the studied samples, the maximum production of hydrogen sulfide was observed using hydrogen as electron donors in the 2, 14 and 15th samples. A high initial content of iron and sulfur was present in the sample 15, and the maximum respiratory activity coefficient was also noted. In the studied samples, the maximum production of hydrogen sulfide was observed using hydrogen as electron donors in the 15th sample. A high initial content of iron and sulfur was present in the sample, and the maximum respiratory activity coefficient was also noted. At the same time, on the 7th sample with a maximum iron content and a low coefficient of microbial fouling, the formation of hydrogen sulfide per month was not recorded.

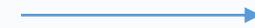
For the final table, a ranking of the synthesis of hydrogen sulfide was carried out and ratings were set: 5 - with an output of 0-0,5 mg, 10 for 0,5-1, 15- 1,-1,5. 20 – 1,5-2.

Biological leaching experiments

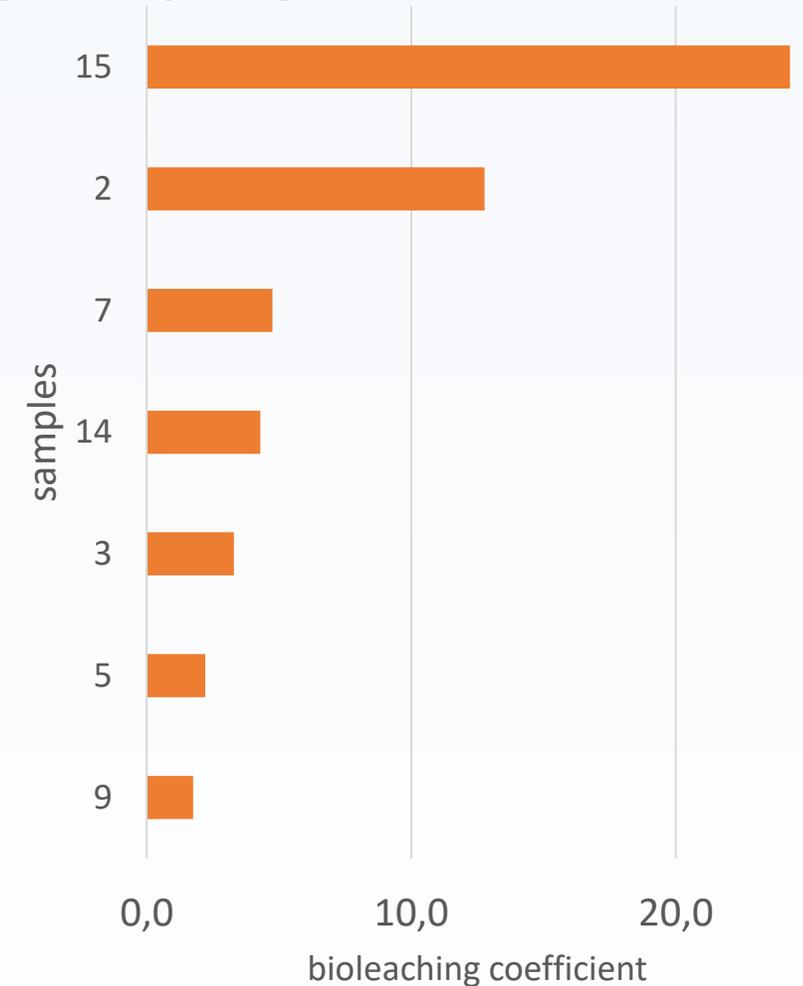
Concentration of the elements in solution after microbial process mg/l

Sample	K	Si	Ca	Al	Fe	Na
2	2,47	4,13	0,72	64,87	1,89	2,55
3	2,14	2,02	1,44	6,22	0,44	7,50
5	2,02	1,98	1,31	2,09	0,13	5,72
7	2,91	2,43	1,28	3,89	16,22	1,77
9	1,38	0,71	0,65	4,63	0,37	5,67
14	1,92	1,87	1,89	16,73	0,87	2,61
15	1,02	9,21	0,33	126,54	7,40	1,40

Biobleaching coefficient



how many times increased the concentration of the all elements (average) in the solution compared to the control



Element concentration was determined by ICP-MS technique

The biological processes of anaerobic conditions in a low mineralized environment without the addition of special electron donors (only that in clay) lead to maximum utilization of the clay mineral resource and leaching of the necessary elements, which leads to partial destruction of clay minerals. Evidence of this is the release of silicon and aluminum phases into the solution. The maximum yield of clay elements during the biological process was observed for samples 15, 2, and 7.

Total table of the clays properties and biosafety

Sample №	Content, mass %				Leached mg/g				MTT Assay coefficient			Biogenic leaching Coefficient*	H2S production mark		*Sum biosafety mark
	Montmorillonite	Fe	S	C	K	Ca	Fe	Σ	Initial OD540	K* _{MTT Ac}	K* _{MTT H2}		*S ²⁻ (Ac)	*S ²⁻ (H2)	
7	78	4,63	0,05	0,14	1,3	5,2	<u>28,8</u>	331,5	1,2	2	1,8	4,8	5	5	19,8
9	89,5	4,82	<0,02	0,01	2,3	6,1	0,6	17,16	0,7	2,7	7,5	2,2	5	5	23,1
3	15	2,29	<0,02	<u>0,68</u>	4,3	40,8	0,23	69,72	1,8	6	8,2	3,3	10	5	34,3
14	67	<u>5,94</u>	<u>0,08</u>	<u>0,86</u>	2,2	13,5	0,33	135,631	0,7	7,2	1,9	4,3	10	10	34,1
5	8	<u>19,94</u>	<0,02	0,19	2,1	15,2	0,28	21,7	1,1	5,4	7,4	2,2	5	20	41,1
2	31	4,54	<0,02	0,41	2,9	5,7	3,5	63,8	0,7	3,5	6,5	12,8	10	10	43,5
15	71	3,36	0,04	0,34	7,3	2,6	2,5	122,66	0,7	17	1,2	24,3	10	10	63,2
corr	-	-	-	+	+-	-	+-	-	-	+	-	+	+	+	+ ¹⁴

Conclusions

In conclusion. We have begun large-scale work to obtain data allowing to penetrate the biological safety of clay barrier materials in the conditions of radioactive waste disposal. Some important correlations have been identified that allow the use of various mathematical methods of calculation and forecasting at the next stages. The work at the initial stage consisted in the search for methodological solutions using a wide range of affordable and relatively inexpensive methods. Of course, the final decision in the selection of methods requires further work and a significantly larger statistical selection of materials. At the moment, our collection has more than 20 different clay materials, including 15 bentonite clays from different deposits of Russia and closest neighbors. We will be happy to expand our base in the framework of cooperation with teams from other countries, and are certainly ready to share our results and experience of our experimental work.